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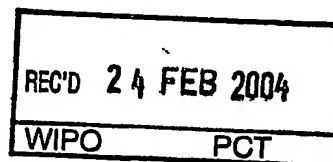
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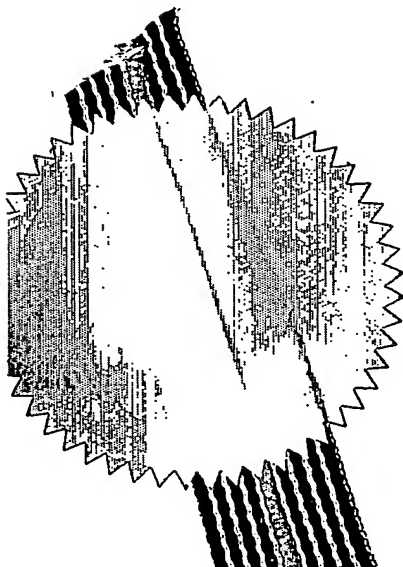
Application forms P.1, P.2, provisional specification
of South African Patent Application No. 2002/7813 as originally filed
in the Republic of South Africa on 30 September 2002 in the name of
BARLOWORLD PLASCON S.A (PTY) LIMITED for an invention entitled:
"VESICULATED POLYMER PARTICLES".

Geteken te
Signed at **PRETORIA**

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

dag van
6th February 2004
day of

1 Registrar of Patents



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FORM P2 (IN DUPLICATE)

REPUBLIC OF SOUTH AFRICA	REGISTRAR OF PATENTS	PATENTS ACT, 1978
OFFICIAL APPLICATION NO : 2002/7813	LODGING DATE : PROVISIONAL	ACCEPTANCE DATE
INTERNATIONAL CLASSIFICATION : LODGING DATE : COMPLETE	GRANTED DATE	
FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)		
BARLOWORLD PLASCON S.A. (PTY) LIMITED		

APPLICANTS SUBSTITUTED:

71	
ASSIGNEE(S)	
71	

DATE REGISTERED

FULL NAME(S) OF INVENTOR(S)

JOHN FRANCIS ENGELBRECHT, BULATHSINDHALAGE BOYD COORAY, DEON DE WET-ROOS, AND ALBERTUS CHRISTIAAN SMIT. ~~AND JOHANNES HENDRIK KNOETZE~~

PRIORITY CLAIMED	COUNTRY	NUMBER	DATE
NB. Use International abbreviation for country (See Schedule 4)	33 N/A	31	32

TITLE OF INVENTION

54|
VESICULATED POLYMER PARTICLES

ADDRESS OF APPLICANT(S)/APPLICANTS

10 Frederick Cooper Drive, Fectoria, Krugersdorp, 1739

ADDRESS FOR SERVICE

74| MORRISON FORSTER INC. P O BOX 2004 MOUNT EDGECOMBE 4300

REF.

556411

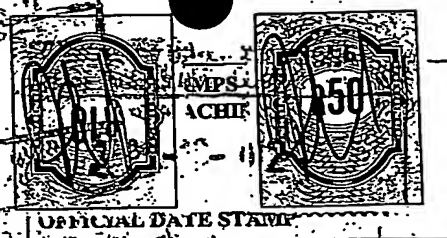
DATE REGISTERED

PATENT OF APPLICATION NO.	DATE OF ANY CHANGE
61	
FRESH APPLICATION BASED ON	DATE OF ANY CHANGE

FORM P.1.
(in duplicate)

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

APPLICATION FOR A PATENT
AND ACKNOWLEDGMENT OF RECEIPT
(SECTION 30(1) - REGULATION 25)



The grant of a patent is hereby requested by the undermentioned application on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

(i) OUR REFERENCE

21 **2002/7813** 556 411

(ii) FULL NAME(S) OF APPLICANT(S)

71. **BARLOWORLD PLASCON S.A. (PTY) LIMITED**

(iii) ADDRESS(ES) OF APPLICANTS

10 Frederick Cooper Drive, Fatoria, Krugersdorp, 1739

(iv) TITLE OF INVENTION

54 **VESICULATED POLYMER PARTICLES**

(v) PRIORITY IS CLAIMED AS SET OUT ON THE ACCOMPANYING FORM P.2.

(vi) THIS APPLICATION IS FOR A PATENT OF ADDITION OF PATENT APPLICATION NO.

21 OI

(vii) THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.

21 OI

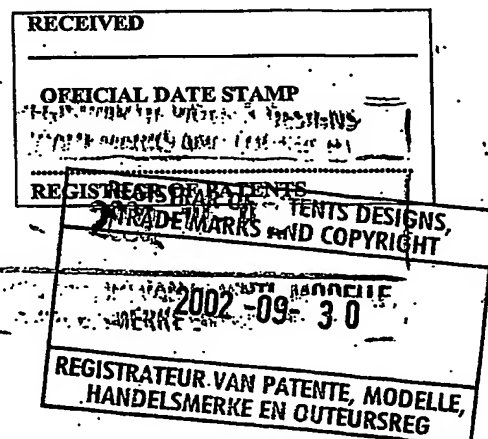
(viii) THIS APPLICATION IS ACCOMPANIED BY

XX	1. A single copy of a provisional specification of 9 pages
	2. Drawings of sheets
	3. Publication particulars and abstract (form P.8 in duplicate)
	4. A copy of Figure of the drawings (if any) for the abstract.
	5. Assignment of invention
	6. Certified priority document(s) (State number)
	7. Translation of the priority document(s)
	8. An assignment of priority rights.
XX	9. A copy of the form P. 2
	10. A declaration of power of attorney on form P.3.
	11. Request for ante-dating on form P.4
	12. Request for classification on form P.9
	13

(ix) ADDRESS FOR SERVICES : **MORRISON FORSTER INC. P O BOX 2004 MOUNT EDGECOMBE 4300**

Dated this 30 day of September 2002

[Signature]
MORRISON FORSTER INC.
APPLICANT'S PATENT ATTORNEYS



FORMP6

MORRISON FORSTER INC.

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
PROVISIONAL SPECIFICATION
(Section 30 (1) - Regulation 27)

OFFICIAL APPLICATION NO

LODGING DATE

OUR REFERENCE

21 **8002/7813**

22 **2002-03-30**

556 411

FULL NAME(S) OF APPLICANT(S)

71 **BARLOWORLD PLASCON S.A. (PTY) LIMITED**

FULL NAME(S) OF INVENTOR(S)

72 **JOHN FRANCIS ENGELBRECHT, ^{CORRECTIONS} BULATHINILAL AGE BOYD COORAY,
DEON DE WET-ROOS, ~~AND~~ ALBERTUS CHRISTIAAN SMIT AND
JOHANNES HENDRIK KNOETZE 16-10-02**

TITLE OF INVENTION

54 **VESICULATED POLYMER PARTICLES**

FIELD OF THE INVENTION

This invention relates to vesiculated polymer particles and a method of manufacture thereof, with particular relevance to their use in coating compositions.

BACKGROUND OF THE INVENTION

The use of vesiculated polymer particles as opacifying agents in coating compositions is well documented in technical and patent literature. These particles have been described as either having a plurality of discrete vesicles or, if manufactured differently, an open, porous structure.

Vesiculated particles are thermosetting polymers for example, cross-linked polyester particles which are formed by encapsulating water in the highly cross-linked polymer. When the water evaporates upon drying, the particle is left with multiple air voids which scatter light randomly giving these particles opacity.

The dispersion of particulate solids, for example pigments, within the individual vesicles to improve the opacifying effect of the vesiculated particles has also been described. Pigment may also be dispersed throughout the polymer phase of which the vesiculated particles are constituted.

Some prior art vesiculated particles have the ability to impart matt or textured finishes on coating compositions when included therein, but cannot be used for gloss finishes. Alternative compositions, for example single vesicle opaque polymer particles, (for example the ROPAQUE range trade mark) are unsuitable for use in matt finishes where low gloss and touch up properties are of paramount importance.

The suitability for imparting matt or gloss finishes to the coating compositions in which they are used, is directly related to the particle size of the vesiculated polymer particles. It is one major disadvantage of prior art manufacturing process that particle size is extremely difficult to control and the attainment of uniform particle sizes or a uniform spread of particle sizes

has not been possible with any great degree of success. This is particularly true at the lower end of the size spectrum where sub-micron sized particles are concerned.

Control of physical processes and in particular agitation, have enjoyed limited success, but chemical control of the process has not been possible.

Apart from the lack of versatility in the manufacturing process of the vesiculated particles and in the limited versatility of end use of the vesiculated particles thus produced, some of these particles also impart poor wet hiding properties in coating compositions. The compositions may also exhibit poor mechanical properties including scrub ability as well as excessive water absorption.

It is therefore an object of this invention to provide vesiculated particles which are more uniform in properties, for example size, than prior art products and which further exhibit improved wet hiding properties, decreased water absorption properties and improved mechanical strength.

It is a further object of the invention to provide a method of manufacture of vesiculated particles which is more versatile, and more easily controlled by both physical and chemical variations in the process. In particular it is an object of the invention to provide a process capable of providing predetermined particle sizes or size spreads from sub-micron size upwards.

THE INVENTION

According to the invention, vesiculated polymer particles include particulate solids and have, associated with the surfaces thereof, long chain aliphatic chemical groups or sterically hindered, branched, chained chemical groups.

In the preferred form of the invention, the particulate solids comprise pigment particles, for example titanium dioxide. Also in the preferred form, the aliphatic groups comprise hydrophobic chemical groups, for example long chain methacrylates. Sterically hindered

groups are preferably also hydrophobic and examples are acrylated or methacrylated castor oil.

In this description, the term associated may refer to groups included in the polymer particles or applied to the surface or portions of the surface thereof.

According to a second aspect of the invention, a method of manufacture of vesiculated polymer particles as described above involves the co-polymerisation of a highly reactive, carboxylated, unsaturated polyester with a reactive monomer, typically an ethylenically unsaturated monomer, as well as a second monomer having hydrophobic properties. The co-polymerisation is preferably a suspension polymerization but could involve other polymerization kinetic mechanisms.

In one example, a method of the invention includes the steps of

- pre-dispersing pigment particles in a polyester;
- dissolving the pre-dispersed pigment-polyester in a suitable monomer in the presence of a water-soluble base;
- forming a stable emulsion of droplets of solution of the pre-dispersed pigment-polyester and monomer (oil phase) in water;
- adding a hydrophobic monomer and polymerising the polyester and co-polymerisable monomer thereby producing granules of opaque, cross-linked vesiculated particles as a colloidal dispersion in water, the particles including hydrophobic groups associated with their surfaces.

In one form, the base may comprise a polyamine, for example diethylenetriamine.

Particles of various sizes may be manufactured using different mixers with different mixing intensity when emulsifying the polyester in water. In one form of the invention, suitably designed equipment controlling pressure, temperature, and residence time, for example homogenisers, may be used. Chemical control of particle size and particle size distribution is

also effected by the introduction of long chain aliphats or sterically hindered, branched, chained co-monomers.

The following examples are intended to illustrate the invention, but are not presented as limitations on the scope of the invention:

Example 1.1

Preparation of vesiculated particles for use in coating compositions which exhibit improved wet hiding capabilities.

A high-speed disperser is used to disperse Tioxide TR81 in a selected polyester resin containing phthalic anhydride and maleic anhydride. Styrene and diethylene triamine (DETA) are added while stirring. This is added to a mixture of polyvinyl alcohol and hydroxyethyl cellulose to which has been added chilled water (10 degrees Celsius) and DETA. The mixture is stirred under controlled pH, temperature, stirring intensity and time conditions until the polyester phase has taken up between 16% and 20% of water. Polymerisation initiator in the form of dissolved Ferrous sulphate and cumene hydroperoxide is added while stirring. The temperature is permitted to rise exothermically to 50 degrees Celsius at which temperature the batch is held for 4 hours. Acticide HF and Disponsil SUS 87 are added while stirring. The result is a colloidal dispersion of vesiculated particles in water.

Example 1.2

As per above but the Tioxide TR81 is omitted.

Results 1

Wet opacity is measured on a draw-down on a Morest Chart using a reflectometer.

Example 1.1 0,83

Example 1.2 0,65

(the higher the figure the higher the opacity).

Example 2.1

Preparation of vesiculated particles for use in coating compositions which exhibit improved scrub resistance and water resistance.

A high-speed disperser is used to disperse Tioxide TR81 in a selected polyester resin containing phthalic anhydride and maleic anhydride. Styrene and diethylene triamine (DETA) are added while stirring. This is added to a mixture of polyvinyl alcohol and hydroxyethyl cellulose to which has been added chilled water (10 degrees Celsius) and DETA. The mixture is stirred under controlled pH, temperature, stirring intensity and time conditions until the polyester phase has taken up between 16% and 20% of water. Polymerisation initiator in the form of dissolved Ferrous sulphate and cumene hydroperoxide is added while stirring. The temperature is permitted to rise exothermically to 50 degrees Celsius at which temperature the batch is held for 4 hours. Acticide HF and Disposil SUS 87 are added while stirring. The result is a colloidal dispersion of vesiculated particles in water.

Example 2.2

As per above but lauryl methacrylate is added as part replacement for styrene.

Method of scrub resistance

Wet scrub (abrasion) resistance is done on a 75 micron wet film thickness of a waterbased paint at 84% pigment volume concentration on a glass panel and allowed to dry for 7 days.

Three paints were evaluated, *i.e.*

- a) Paint containing no vesiculated particles
- b) Paint containing 19% vesiculated particles as per Example 2.1 (wet vesiculated bead on wet paint by mass).
- c) Paint containing 19% vesiculated particles as per Example 2.2 (wet vesiculated bead on wet paint by mass).

Results 2

	<u>Scrub Cycles</u>
Paint a) above	1269
Paint b) above	598
Paint c) above	2198

Method for water resistance evaluation

Paint b) and Paint c) above are supplied on glass at 75 micron wet film thickness and allowed to dry for 24 hours.

Water drops are applied to the paint and observed for softening, blistering and wrinkling. The time is recorded when the defects occur. Ten minutes is the maximum time used in the test.

Results 2

Paint b)	2 minutes
Paint c)	> 10 minutes

Example 3.1

Preparation of vesiculated particles for use in coating compositions which exhibit reduced particle size and narrow particle size distribution by process control.

A high-speed disperser is used to disperse Tioxide TR81 in a selected polyester resin containing phthalic anhydride and maleic anhydride. Styrene and diethylene triamine (DETA) are added while stirring. This is added to a mixture of polyvinyl alcohol and hydroxyethyl cellulose to which has been added chilled water (10 degrees Celsius) and DETA. The mixture is stirred under controlled pH, temperature, stirring intensity and time conditions until the polyester phase has taken up between 16% and 20% of water. Polymerisation initiator in the form of dissolved Ferrous sulphate and cumene hydroperoxide is added while stirring. The temperature is permitted to rise exothermically to 50 degrees Celsius at which temperature the batch is held for 4 hours. Acticide HF and Disposil SUS

87 are added while stirring. The result is a colloidal dispersion of vesiculated particles in water.

Example 3.2

Same as Example 3.1 but using an homogeniser which has much higher mixing intensity.

Method of particle size measurement

A 200 micron wet draw-down is done on a Morest Chart of the vesiculated beads made by Method 3.1 and 3.2 above. The draw-down is allowed to dry for 24 hours and average particle size and particle size distribution is measured on a Scanning Electron Microscope.

Results 3

	<u>Average Particle SizeParticle Size Distribution</u>	
Example 3.1 above	5,0 micron	2,0 - 11,0 micron
Example 3.2 above	0,7 micron	0,1 - 5,0 micron

Example 4.1

Preparation of vesiculated particles for use in coating compositions which exhibit particle size control by chemical means.

A high-speed disperser is used to disperse Tioxide TR81 in a selected polyester resin containing phthalic anhydride and maleic anhydride. Styrene and diethylene triamine (DETA) are added while stirring. This is added to a mixture of polyvinyl alcohol and hydroxyethyl cellulose to which has been added chilled water (10 degrees Celsius) and DETA. The mixture is stirred under controlled pH, temperature, stirring intensity and time conditions until the polyester phase has taken up between 16% and 20% of water. Polymerisation initiator in the form of dissolved Ferrous sulphate and cumene hydroperoxide is added while stirring. The temperature is permitted to rise exothermically to 50 degrees Celsius at which temperature the batch is held for 4 hours. Acticide HF and Disposil SUS 87 are added while stirring. The result is a colloidal dispersion of vesiculated particles in water.

Example 4.2

As per above but lauryl methacrylate is added as part replacement for styrene.

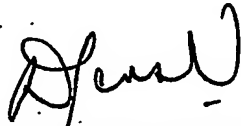
Method for measuring particle size

As given in Example 3.

Results 4Average Particle SizeParticle Size Distribution

Example 4.1 above	5,0 micron	2,0 - 11,0 micron
Example 4.2 above	11,0 micron	5,0 - 33,0 micron

Dated this 30 day of September 2002



MORRISON FORSTER INC.
APPLICANTS' PATENT ATTORNEYS

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